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Te[illegible]Report S[illegible]on the B[illegible]osystem-A[illegible]sphere Study (BOREAS)

[illegible]ll and Sara K. Conrad, Editors

[illegible] 243

[illegible]AS TGB-10 Volatile Organic [illegible]he SSA

[illegible], B. Hall, A.V. Jackson

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Technical Report Series on the Boreal Ecosystem-Atmosphere Study (BOREAS)

Forrest G. Hall and Sara K. Conrad, Editors

Volume 243

BOREAS TGB-10 Volatile Organic Carbon Data over the SSA

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BOREAS TGB-10 Volatile Organic Carbon Data over the SSA

Hal Westberg, Brad Hall, Andrea V. Jackson

Summary

The BOREAS TGB-10 team collected several trace gas data sets in its efforts to determine the role of biogenic hydrocarbon emissions with respect to boreal forest carbon cycles. This data set contains measured VOC concentrations. These data were obtained at the SSA-OJP site from May to September 1994. The data are stored in tabular ASCII files.

Table of Contents

1. Data Set Overview

1.1 Data Set Identification

BOREAS TGB-10 Volatile Organic Carbon Data over the SSA

1.2 Data Set Introduction

The BOReal Ecosystem-Atmosphere Study (BOREAS) Trace Gas Biogeochemistry (TGB)-10 team collected Volatile Organic Carbon (VOC) concentration data at the Southern Study Area (SSA) Old Jack Pine (OJP) site during the growing season of 1994. The equipment used included Teflon bags, 6-liter passivated stainless steel canisters, and a gas chromatograph. A combination of branch enclosures and gradient and Relaxed Eddy Accumulation (REA) methods were used to make the needed measurements.

1.3 Objective/Purpose

Emission/deposition rates of biogenic hydrocarbons (or VOC) were measured along with ambient concentrations of biogenic hydrocarbons. We will use these data to examine (a) the role of biogenic hydrocarbon emissions with respect to carbon cycles in the boreal forest, (b) the chemical fate of boreal biogenic emissions, (c) the hypothesis that biospheric VOC emissions contribute to peroxide formation, and (d) the deposition rates of hydrogen peroxide and organic peroxides.

1.4 Summary of Parameters

Investigations of biogenic hydrocarbon emissions and tropospheric concentrations of hydrogen peroxide and organic hydroperoxides in a boreal forest.

1.5 Discussion

None given.

1.6 Related Data Sets

BOREAS TGB-08 Monoterpene Concentration Data over the SSA
BOREAS TGB-08 Starch Data over the SSA
BOREAS TGB-08 Photosynthesis Data over the SSA
BOREAS TGB-09 Above Canopy Non-Methane Hydrocarbon Data over the SSA

2. Investigator(s)

2.1 Investigator(s) Name and Title

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Washington State University

Dr. Nick Hewitt
Lancaster University

2.2 Title of Investigation

Measurement of Biogenic Hydrocarbon Fluxes

2.3 Contact Information

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3. Theory of Measurements

Three different methods were employed to measure biogenic VOC fluxes in the BOREAS SSA. A branch enclosure technique provided individual branch-level emission estimates. Tower-based gradient and REA methods yielded canopy-scale biogenic hydrocarbon fluxes.

Enclosure Method:

Hydrocarbon emission rates were determined using a dynamic enclosure technique. The emission rate was calculated from the following expression:

$E = C*Q/B$ (g C/g/s)

where C (g C/m^3) (g C (g C/m^3) (g C is grams carbon) is the concentration of a specific hydrocarbon, Q (m^3/s) is the flow rate of air through the chamber, and B (g) is the dry leaf (needle) biomass of the enclosed branch.

Gradient Method:

Canopy-scale biogenic hydrocarbon fluxes and hydrogen peroxide deposition velocities were determined by the flux-gradient technique, in which the flux is expressed as the product of an eddy exchange coefficient and the concentration gradient. The biogenic VOC flux (F) can be derived from the eddy exchange coefficient and the measured gradient.

$F = K*(dC/dz)$ (g C/m^2/s)

where K (m^2/s) is an eddy diffusion coefficient and concentration is measured in gC/m^3.

The deposition velocity (Vd) of hydrogen peroxide is found from the eddy exchange coefficient and the normalized gradient.

$Vd = K*(dC/dz)/C$ (m/s)

where concentration is measured in ppbV.

REA Method:

Canopy-scale fluxes of biogenic hydrocarbons were determined by the REA method at the Old Black Spruce (OBS) site. These measurements were carried out in cooperation with Dr. Elizabeth Pattey (BOREAS Tower Flux (TF)-07 team). In this method, air is sampled at a constant rate and partitioned into one of two containers, contingent upon whether the vertical velocity component was positive (upward) or negative (downward). The flux is computed from the following expression:

$F = b*sw*(C2 - C1)$ (g C/m^2/s)(g C/m^2/s)

where b (dimensionless) is a weak function of stability (determined by eddy correlation measurements of heat, water vapor, or CO_2 flux), sw (m/s) is the standard deviation of vertical wind speed, and C2 and C1 (g C/m^3) are the concentrations in the "upward" and "downward" containers, respectively. For a more complete description of the REA method, one should consult the TF-07 documentation.

Hydrogen Peroxide Measurements (TGB-10b):

Hydrogen peroxide (BOREAS TGB-10b) was measured by the continuous, enzyme-catalyzed, fluorometric method (Lazrus et al., 1986). An incoming air stream (2 L/min) was split equally into two parts. Each gas stream was passed through a glass stripping coil in which peroxides were dissolved into a buffer solution at pH 5.8 (0.5 mL/min, 0.004 M potassium hydrogen phthalate). To each liquid stream (A and B), horseradish peroxidase (8,000 units/L, type II, Sigma Chemical), 0.004 M p-hydroxyphenylacedic acid (POPHA), 0.004 M ethylenediamine tetraacetic acid (EDTA), and 0.0005 M formaldehyde (HCHO) solutions were added. Prior to the addition of the peroxidase and POPHA, bovine-liver catalase, which destroys hydrogen peroxide, was added to stream B. The catalase concentration is adjusted until approximately 90% of the H_2O_2 in channel B is destroyed. In both channels, peroxidase catalyzes the reaction of peroxides with POPHA to form a fluorescent dimer with excitation and emission wavelengths of 320 and 400 nm, respectively. The resulting signals, generated by photomultiplier tubes, are proportional to the peroxide concentration in each photo cell. Hydrogen peroxide concentration is the difference in signal between channels A and B.

Air was sampled at each height through a 4-meter section of 1/4" PFA Teflon tubing connected to a PFA Teflon-coated 2-way valve (Furon). From there, the air was drawn through 40 m of PFA Teflon line to the analytical system, located inside the instrument hut. At this point, the air stream was separated into two streams by a PFA Teflon tee. One stream was sent to the hydrogen peroxide instrument and the other to the ozone analyzer. The valve was switched at 18-minute intervals, sequentially sampling air at both levels.

Hydrogen Peroxide and Organic Hydroperoxide Measurements (TGB-10c):

Ambient hydrogen peroxide and organic hydroperoxides concentrations were determined by high performance liquid chromatography (HPLC) with fluorometric detection. The detection method is similar to that described in the previous section. Air was drawn at 4 L/min from the inlet (24 m height) on the TF tower through 1/4" TFE Teflon tubing to the tower base, where a gas-phase scrubber was used to scrub peroxides from the air stream. Samples were collected in 5 mL deionized water. HPLC analysis was performed immediately after sample collection.

HPLC separation was achieved on an Absorbosphere MF Plus C18 column (Altech) with an eluent of 0.001 M sulfuric acid with 0.0001 M EDTA delivered by a Merck-Hitachi L-6200 Intelligent HPLC pump at a flow rate of 0.6 mL/min. After separation, the peroxides were derivatized by addition of 0.026 M p-hydroxyphenylacetic acid with 10,000 units/L of horseradish peroxidase (type II Sigmal Chemical) in 0.5 M potassium hydrogen phthalate buffer at pH 5.8. The reaction of the fluorescence reagent with the separated hydroperoxides takes place in a Teflon coil to ensure adequate mixing. Following this, the pH of the resulting solution is raised to above 10 to convert the dimer to its fluorescent anionic form using a membrane reactor constructed of Nafion (DuPont) tubing immersed in

30% ammonium hydroxide solution. Fluorescence measurements were made using a Merck-Hitachi spectrophotometer with excitation and emission wavelengths of 310 and 405 nm, respectively. The HPLC analytical system was located in the instrument hut.

Formaldehyde Monitoring:

The reaction of formaldehyde with dinitrophenylhydrazine (DNPH) was the basis for the measurement procedure used during this study. A DNPH/silica cartridge was connected to the inlet end of a 1/4" stainless steel tube extending to 3 m above the ground. The sample flow (1 L/min) was generated with a small pump and monitored with a Matheson flow meter. A calibrated Tylan digital totalizer was used to record the total volume sampled. The cartridges were exposed to the ambient air for nominal durations of 2, 4, or 6 hours. Cartridges were brought back to Washington State University (WSU) for analysis.

Sample and blank cartridges were eluted with 3 mL acetonitrile. Hydrazone concentrations in the eluent were determined by reverse-phase HPLC. The HPLC analysis was performed using a LKB modular system consisting of two pumps (LKB #2150), a 190-600 nm ultraviolet/visible wavelength detector (LKB #2151) operated at 360 nm, and an LC gradient controller (LKB # 2152). A Brownlee-Rainin 10-cm OD-MPS column (or comparable) with a hydrophobic, nonpolar stationary phase (bonded on 5-micrometer spheres), preceded by a similar guard column was used for peak separation. A gradient elution, beginning with a 50:50 water:acetonitrile ratio was used, changing to a 30:70 water:acetonitrile ratio over a period of 21 minutes. The column flow rate was 0.5 mL/min and the sample loop volume was 20 microliters.

4. Equipment

4.1 Sensor/Instrument Description

Biogenic VOCs:

Biogenic VOC samples were analyzed on a Hewlett Packard HP5890 gas chromatograph fitted with a cryogenic accessory and two flame ionization detectors. A freeze-out trap was used with a six-port gas sampling valve for preconcentrating the sample prior to injection. A 30-m DB-1 fused silica column was used in a temperature-programmed mode (-50 deg C to 150 deg C at 4 deg/min) to separate VOCs in the C5 to C10 range. Compound identities were determined through retention time comparisons and mass spectral analysis. Sample volume was measured with a vacuum system employing an evacuated vessel of known volume and a digital vacuum gauge (Validyne). Sample volumes range from 100 to 1,000 cm^3 depending upon the expected VOC concentration.

Gradient samples for biogenic VOCs were collected in 6-liter passivated stainless steel canisters. The sample containers were cleaned prior to field deployment by heating under reduced pressure, and then flushed with humidified, hydrocarbon-free air at room temperature. REA samples were collected in Teflon bags. Immediately after filling, the contents of the bag were transferred to a stainless steel canister for transport to the analytical laboratory.

Hydrogen Peroxide:

Hydrogen peroxide (TGB-10b) was measured by the dual-channel, enzyme-catalyzed, fluorometric method. The instrument was constructed at WSU, following the procedure outlined by K&K Instruments; Boulder, Colorado (Lazrus et al., 1986).

Ozone:

Ozone was measured with a Dasibi 1003-AH ozone sensor.

4.1.1 Collection Environment

Tower-based measurements were conducted under ambient atmospheric conditions. Enclosure-based biogenic VOC measurements were conducted under near-ambient conditions, but at slightly elevated temperatures.

4.1.2 Source/Platform

All biogenic VOC, peroxide, and ozone measurements were made from ground- or tower-mounted instruments.

4.1.3 Source/Platform Mission Objectives

The objective of these experiments was to obtain canopy-scale fluxes of biogenic VOCs and peroxides, and branch-scale fluxes of biogenic VOCs in a boreal environment.

4.1.4 Key Variables

Emissions and/or ambient concentrations of the following trace gases were measured:

- isoprene
- alpha-pinene
- beta-pinene
- limonene
- monoterpenes
- hydrogen peroxide
- methylhydroperoxide
- hydroxymethlyhydroperoxide
- ozone

4.1.5 Principles of Operation

See Section 3.

4.1.6 Sensor/Instrument Measurement Geometry

Enclosure Sampling:

The instruments used for enclosure sampling were mounted on a battery-powered portable cart. The bag enclosure was mounted on a tripod base, allowing access to branches 1-3 meters from the ground.

Biogenic VOC Analysis:

The gas chromatographic system was housed in the WSU mobile lab, located at the Torch Camp site (Highway 120, near the Torch River). This central location served to minimize the storage time for VOC samples.

Gradient Sampling:

Inlets were located on beams protruding 1 m off the west sides of the TF towers. With winds predominately from the south, west, or north, the samples usually contained unperturbed air. The inlet heights (above the forest floor) are summarized below.

```
Old Aspen (OA)    27.5 m and 37.5 m
OBS               12.4 m and 23.3 m
OJP               16.5 m and 23.8 m   Intensive Field Campaign (IFC)-1, IFC-2
OJP               17.2 m and 23.8 m   IFC-3
```

The lower inlet at the OJP site was raised prior to IFC-3 to alleviate possible influences of the roughness sublayer.

4.1.7 Manufacturer of Sensor/Instrument

HP5890 gas chromatograph:
Hewlett Packard
15815 SE 37th St.
Bellevue, WA 98006

Dasibi 1003-AH ozone analyzer:
Dasibi Environmental
616 E. Colorado St.
Glendale, CA 91205

HP-3396A integrator:
Hewlett Packard
15815 SE 37th St.
Bellevue, WA 98006

The hydrogen peroxide system was custom-built at WSU:
WSU Technical Services
Washington State University
Pullman, WA 99164-2801

HPLC system (TGB-10c):
Merck Ltd.
Merck House
Poole, Dorset
BH15 1TD, England

Data handling systems:
Labtech
400 Research Dr.
Wilmington, MA 01887

VG Data Systems
St. Georges Court
Hanover Business Park
Altrincham, Cheshire
WA14 5UG England

4.2 Calibration

4.2.1 Specifications

Hydrogen Peroxide:

The H_2O_2 gradient measurements were occasionally subject to bias. It was extremely difficult to maintain clean sampling conditions at all times. Inlet filters cannot be used due to the potential for severe H_2O_2 loss on filter surfaces.

Periods of unacceptable bias were encountered during the first IFC when the jack pine trees were pollinating, and occasionally during IFC-2 and IFC-3 when bugs would collect in the sample lines. The sample lines were sequentially flushed with methanol, water, and dry air periodically to remove dirt, pollen, and bugs.

Ozone:

Calibration of the gas chromatograph was achieved by measuring instrument response to a known concentration of 2,2-dimethylbutane in air (Scott Environmental Technology; cylinder # A-11). The resulting calibration curves have been compared to a propane standard that is traceable to the National Institute for Standards and Technology (NIST, formerly NBS) (3.08 ppm propane; ID# M3281665). Daily span checks were performed during each field campaign using the 0.204 ppm 2,2-dimethylbutane standard.

Formaldehyde:

High-purity formaldehyde-hydrazone was prepared by conventional methods for use as a master standard. The master standard was diluted to concentrations of 0.2, 0.5, 1.0, 2.0, and 5.0 ppm to establish calibration curves.

Sensors for the peripheral environmental measurements were calibrated at WSU prior to the field sampling program. Mass flow meters were tested against a precision wet-test meter at several flow rates. The thermocouples and amplifiers were calibrated against a NIST traceable mercury thermometer by measuring the response with all sensors immersed in a stirred ice-water bath slowly warmed to approximately 45 deg C. The humidity sensor was compared to calculated values for air passed through a temperature-controlled water bath. All of the sensor calibrations were performed using the PC laptop data system employed in the field.

4.2.1.1 Tolerance

None given.

4.2.2 Frequency of Calibration

Calibrations were performed before and after each IFC. Bias checks for peroxide gradients were performed every few days during IFC-2 and IFC-3. No bias checks were performed during IFC-1.

4.2.3 Other Calibration Information

Hydrogen peroxide (TGB-10b):

The continuous hydroperoxide system was calibrated twice daily with liquid standards of hydrogen peroxide in deionized water. The standards were prepared at the 10-8 M level by serial dilution of a 30% H_2O_2 reagent (Fisher). The concentration of the primary reagent was determined by titration against $KMnO_4$, which was then titrated against a NIST traceable sodium oxalate solution.

Line losses through the PFA Teflon tubing were measured before and after each IFC. A gas-phase H_2O_2 generation system was used to produce a sample stream with near-ambient levels of H_2O_2. Line losses were determined by sampling this stream with and without the tower sampling line. A critical aspect of the peroxide gradient system is the potential for bias introduced in the two separate inlet sections. Care was taken to ensure that bias introduced by the valve and 4-m inlet sections was well-known and correctable. Relative bias was determined every few days by placing both inlets at the same height and sampling ambient air for several hours. Subsequent gradients were corrected for bias, which ranged from -1 to 9%. When the bias surpassed 7%, samples were rejected and the valve and sample lines were cleaned with methanol, deionized water, and peroxide-free air. After cleaning, bias was reduced to a nondetectable level.

Hydroperoxides (TGB-10c):

Peak identities were confirmed by comparison with retention times of authentic standards. Quantification was based on system response to hydrogen peroxide, as the same fluorescent dimer is formed for all hydroperoxides. Calibration was carried out twice daily and was found to be linear over the range $8x10^{-8}$ M to $5x10^{-6}$ M. The limit of detection has been determined to be less than 50 pptv.

Ozone:

The Dasibi ozone monitor was calibrated against a Dasibi ozone source/monitor model 1008-PC (serial #3226).

5. Data Acquisition Methods

Enclosure Method

The enclosure consisted of a cylindrical 30-liter Teflon film bag supported externally supported on a metal frame. Hydrocarbon-free zero air (from a compressed gas cylinder) was swept through the Teflon bag at a controlled rate. The zero air "sweep gas" was introduced through a perforated annular ring at one end and exhausted through a port at the other end. The sweep gas was humidified by bubbling through a water bath, maintained at ambient temperature. Carbon dioxide was added to yield near-ambient CO_2 concentrations (360 +/- 10 ppm) in the sweep gas.

Gradient Method

Ambient concentrations of biogenic hydrocarbons were measured at two heights (see Section 4.1.6) above the OBS, OA, and OJP forests. Hydrogen peroxide was measured at two heights above the OJP forest. For biogenic hydrocarbons, 30-minute average concentrations were determined by simultaneously filling two stainless steel canisters. Each canister was connected to a PTFE Teflon line running from a location on the tower (above the canopy) to the tower base. For hydrogen peroxide, the concentration at each height was measured sequentially at 18-minute intervals. The average concentrations observed during each interval were used to compute the concentration gradient. Eddy exchange coefficients for heat and water vapor were determined by simultaneously measuring the fluxes (by eddy correlation) and the gradients of heat and water vapor. The respective TF groups will provide these data.

REA Method

Canopy-scale fluxes of biogenic hydrocarbons were determined by the REA method at the OBS site. In this method, air is sampled at a constant rate and partitioned into one of two containers, contingent upon whether the vertical velocity component was positive (upward) or negative (downward).

Signals from the hydrogen peroxide and ozone instruments (TGB-10b) were stored as 1-minute averages via PC computer. Data acquisition software from Labtech was used to record signals (voltages).

The gas chromatograph was interfaced to a pair of HP-3396A integrators for peak integration. Raw signals were also stored via PC computer for data reprocessing.

The HPLC system for hydroperoxides was interfaced with a VG Data Systems Minichrom data acquisition system for chromatography. The connection of the HPLC to the data system was achieved using a chromatography server.

6. Observations

6.1 Data Notes

Hydrogen peroxide:

Periods of unacceptable bias were encountered during the first IFC, when the jack pine trees were pollinating, and occasionally during IFC-2 and IFC-3 when bugs would collect in the sample lines.

Ozone:

Some problems with the electronic zero were detected during IFC-1. An offset of -6 ppb relative to the data acquisition system was discovered. This offset was easily measured on a daily basis, and remained essentially unchanged throughout the experiment.

6.2 Field Notes

TGB-10b Peroxide data were deemed questionable (QC = 2) or unacceptable (QC = 3) during the following periods:

```
C *** QUALITY CONTROL (based local TIME and DOY)
IF (DOY .EQ. 145) QC = 2                                   poor calibration
IF (DOY .EQ. 146) QC = 2                                   poor calibration
IF (DOY .EQ. 147) QC = 2                                   poor calibration
IF (DOY .EQ. 155) QC = 3                                   extreme pollen event
IF (DOY .EQ. 156) QC = 3                                   poor calibration
IF (DOY .EQ. 157) QC = 2                                   moderate pollen event
IF (DOY .EQ. 160) THEN
IF (TIME .GT. 17.) QC = 2                                  bias unknown
ENDIF
IF (DOY .EQ. 206) THEN
 IF ((TIME .GT. 8.0) .AND. (TIME .LT. 12.0)) QC = 2        poor calibration
ENDIF
IF (DOY .EQ. 212) THEN
 IF ((TIME .GT. 3.0) .AND. (TIME .LT. 9.0))  QC = 3        high noise level
ENDIF
IF (DOY .EQ. 216) QC = 2                                   None Given.
```

7. Data Description

7.1 Spatial Characteristics

7.1.1 Spatial Coverage

Biogenic VOC fluxes were determined at three tower sites in the SSA (OA, OBS, and OJP). Peroxide and ozone concentrations were measured only at the OJP site. The North American Datum of 1983 (NAD83) coordinates for the sites are:

```
SSA-OA    53.62889N, 106.197779W
SSA-OBS   53.91634N, 104.69203W
SSA-OJP   53.98717N, 105.11779W
```

7.1.2 Spatial Coverage Map

Not available.

7.1.3 Spatial Resolution

These data represent point source measurements at the given locations.

7.1.4 Projection

Not applicable.

7.1.5 Grid Description

Not applicable.

7.2 Temporal Characteristics

7.2.1 Temporal Coverage

Biogenic VOC samples were collected for 30-minute periods. Sampling was usually performed from sunrise to sunset, to capture the diurnal variability. Some overnight sampling was performed at the OA site during IFC-3. Ambient biogenic VOC and oxidation products were measured at the Torch Camp (near Candle Lake, Saskatchewan) during each IFC. These measurements were meant to supplement those obtained at the tower sites.

Peroxide and ozone concentrations were measured continuously during daylight hours. In addition, many overnight sampling periods were obtained.

7.2.2 Temporal Coverage Map

Not available.

7.2.3 Temporal Resolution

No regular intervals of data collection resulted at the sites; however, data were collected on several days during the growing season of 1994 at each location.

7.3 Data Characteristics

7.3.1 Parameter/Variable

The parameters contained in the data files on the CD-ROM are:

```
         Column Name
------------------------------
SITE_NAME
SUB_SITE
DATE_OBS
TIME_OBS
ISOPRENE_CONC
ALPHA-PINENE_CONC
BETA-PINENE_CONC
CAMPHENE_CONC
CRTFCN_CODE
REVISION_DATE
```

7.3.2 Variable Description/Definition

The descriptions of the parameters contained in the data files on the CD-ROM are:

Column Name	Description
SITE_NAME	The identifier assigned to the site by BOREAS, in the format SSS-TTT-CCCCC, where SSS identifies the portion of the study area: NSA, SSA, REG, TRN, and TTT identifies the cover type for the site, 999 if unknown, and CCCCC is the identifier for site, exactly what it means will vary with site type.
SUB_SITE	The identifier assigned to the sub-site by BOREAS, in the format GGGGG-IIIII, where GGGGG is the group associated with the sub-site instrument, e.g. HYD06 or STAFF, and IIIII is the identifier for sub-site, often this will refer to an instrument.
DATE_OBS	The date on which the data were collected.
TIME_OBS	The Greenwich Mean Time (GMT) when the data were collected.

ISOPRENE_CONC	The ambient concentration of isoprene
ALPHA-PINENE_CONC	The ambient concentration of alpha-pinene.
BETA-PINENE_CONC	The ambient concentration of beta-pinene.
CAMPHENE_CONC	The ambient concentration of camphene.
CRTFCN_CODE	The BOREAS certification level of the data. Examples are CPI (Checked by PI), CGR (Certified by Group), PRE (Preliminary), and CPI-??? (CPI but questionable).
REVISION_DATE	The most recent date when the information in the referenced data base table record was revised.

7.3.3 Unit of Measurement

The measurement units for the parameters contained in the data files on the CD-ROM are:

Column Name	Units
SITE_NAME	[none]
SUB_SITE	[none]
DATE_OBS	[DD-MON-YY]
TIME_OBS	[HHMM GMT]
ISOPRENE_CONC	[parts per billion Carbon]
ALPHA-PINENE_CONC	[parts per billion Carbon]
BETA-PINENE_CONC	[parts per billion Carbon]
CAMPHENE_CONC	[parts per billion Carbon]
CRTFCN_CODE	[none]
REVISION_DATE	[DD-MON-YY]

7.3.4 Data Source

The sources of the parameter values contained in the data files on the CD-ROM are:

Column Name	Data Source
SITE_NAME	Not applicable
SUB_SITE	Not applicable
DATE_OBS	Investigator
TIME_OBS	Investigator]
ISOPRENE_CONC	Gas Chromatograph
ALPHA-PINENE_CONC	Gas Chromatograph
BETA-PINENE_CONC	Gas Chromatograph
CAMPHENE_CONC	Gas Chromatograph
CRTFCN_CODE	Not applicable
REVISION_DATE	Not applicable

7.3.5 Data Range

The following table gives information about the parameter values found in the data files on the CD-ROM.

Column Name	Minimum Data Value	Maximum Data Value	Missng Data Value	Unrel Data Value	Below Detect Limit	Data Not Cllctd
SITE_NAME	SSA-9OA-FLXTR	SSA-OJP-FLXTR	None	None	None	None
SUB_SITE	TGB10-HCR01	TGB10-HCR01	None	None	None	None
DATE_OBS	31-MAY-94	09-SEP-94	None	None	None	None
TIME_OBS	0	2340	None	None	None	None
ISOPRENE_CONC	.13	36.23	-9999	None	None	None

```
ALPHA-PINENE_CONC     .049           5.86           -9999   None    None    Blank
BETA-PINENE_CONC      .072           3.65           -9999   None    None    Blank
CAMPHENE_CONC         .055           2.88           -9999   None    None    Blank
CRTFCN_CODE           CPI            CPI            None    None    None    None
REVISION_DATE         06-OCT-95      06-OCT-95      None    None    None    None
---------------------------------------------------------------------------------
Minimum Data Value -- The minimum value found in the column.
Maximum Data Value -- The maximum value found in the column.
Missng Data Value  -- The value that indicates missing data. This is used to
                      indicate that an attempt was made to determine the
                      parameter value, but the attempt was unsuccessful.
Unrel Data Value   -- The value that indicates unreliable data.  This is used
                      to indicate an attempt was made to determine the
                      parameter value, but the value was deemed to be
                      unreliable by the analysis personnel.
Below Detect Limit -- The value that indicates parameter values below the
                      instruments detection limits.  This is used to
                      indicate that an attempt was made to determine the
                      parameter value, but the analysis personnel determined
                      that the parameter value was below the detection
                      limit of the instrumentation.
Data Not Cllctd    -- This value indicates that no attempt was made to
                      determine the parameter value.  This usually
                      indicates that BORIS combined several similar but
                      not identical data sets into the same data base table
                      but this particular science team did not
                      measure that parameter.

Blank -- Indicates that blank spaces are used to denote that type of value.
N/A   -- Indicates that the value is not applicable to the respective column.
None  -- Indicates that no values of that sort were found in the column.
---------------------------------------------------------------------------------
```

7.4 Sample Data Record

The following are wrapped versions of data record from a sample data file on the CD-ROM.

```
SITE_NAME,SUB_SITE,DATE_OBS,TIME_OBS,ISOPRENE_CONC,ALPHA-PINENE_CONC,
BETA-PINEN_CONC,CAMPHENE_CONC,CRTFCN_CODE,REVISION_DATE
'SSA-9OA-FLXTR','TGB10-HCR01',11-JUN-94,1500,4.41,,,,'CPI',06-OCT-95
'SSA-9OA-FLXTR','TGB10-HCR01',11-JUN-94,1700,5.46,,,,'CPI',06-OCT-95
'SSA-9OA-FLXTR','TGB10-HCR01',11-JUN-94,1800,6.71,,,,'CPI',06-OCT-95
'SSA-9OA-FLXTR','TGB10-HCR01',11-JUN-94,1900,3.69,,,,'CPI',06-OCT-95
```

8. Data Organization

8.1 Data Granularity

The smallest unit of data tracked by BORIS was the data measured on a particular day at a particular site.

8.2 Data Format(s)

The Compact Disk-Read-Only Memory (CD-ROM) files contain American Standard Code for Information Interchange (ASCII) numerical and character fields of varying length separated by commas. The character fields are enclosed with single apostrophe marks. There are no spaces between the fields.

Each data file on the CD-ROM has four header lines of Hyper-Text Markup Language (HTML) code at the top. When viewed with a Web browser, this code displays header information (data set title, location, date, acknowledgments, etc.) and a series of HTML links to associated data files and related data sets. Line 5 of each data file is a list of the column names, and line 6 and following lines contain the actual data.

9. Data Manipulations

9.1 Formulae

The peroxide gradient was computed from 3 successive measurements of peroxide concentration at two levels (10-18 minutes at each level).

Peroxide_gradient = (C2 - 0.5*(C1+C3))/delta_Z

where: C1 = concentration measured at lower level (period t)
C2 = concentration measured at upper level (period t+1)
C3 = concentration measured at lower level (period t+2)

Special note: If the standard error associated with C1, C2, or C3 was greater than 0.05%,the peroxide gradient was deemed unacceptable. This procedure was performed in order to screen periods of highly variable concentration, which might suggest unsteady-state conditions (gusts or large eddies) which are not conducive to K-theory.

9.1.1 Derivation Techniques and Algorithms

None given.

9.2 Data Processing Sequence

9.2.1 Processing Steps

BORIS staff processed the data by:

- Reviewing the initial data files and loading them online for BOREAS team access.
- Designing relational data base tables to inventory and store the data.
- Loading the data into the relational data base tables.
- Working with the Hydrology (HYD)-06 team to document the data set.
- Extracting the standardized data into logical files.

9.2.2 Processing Changes

None given.

9.3 Calculations

Emission rate:

E = C*Q/B

where: C is the concentration of a specific VOC
Q is the flow rate of air through the chamber
B is the dry leaf (needle) biomass of the enclosed branch

Biogenic VOC flux (F):

F = K*(dC/dz)

Deposition velocity (Vd):

$$Vd = K*(dC/dz)/C$$

9.3.1 Special Corrections/Adjustments

Peroxide Bias adjustment: $C1 = C1*fb \quad C3 = C1*fb$

where: fb = bias relative to upper sampling level
(range 0.99 to 1.07 for H2O2, 0.99 to 1.02 for ROOH)

9.3.2 Calculated Variables

None given.

9.4 Graphs and Plots

None.

10 Errors

10.1 Sources of Error

Hydrogen Peroxide (TGB-10b): The following sources of error are those that are not easily identified, and may affect the data record despite efforts to identify and correct all errors.

- Irregularities in sample line loss (condensation, dirt, bugs).
- Contamination of the switching valve due to bugs, dirt, pollen, etc.
- Irregular signal drift, possibly due to extreme temperature fluctuations.
- Interference due to smoke particles.

Hydroperoxides (TGB-10c):

- Fluctuations in air flow rate.
- Error in preparing sample volume.
- Fluctuations in sample collection efficiency with temperature.
- Possible condensation in sample lines.
- Interference due to smoke particles.
- Error associated with the serial dilution of H_2O_2 standards.

10.2 Quality Assessment

10.2.1 Data Validation by Source

None given.

10.2.2 Confidence Level/Accuracy Judgment

Hydrogen peroxide concentrations are good to approximately 30%. Total organic peroxide concentrations have not been corrected for collection efficiency. Reported total organic peroxide concentration may be underestimated by as much as 60%. Individual deposition velocity measurements are subject to 50-80% uncertainty due to uncertainties in the measured gradient, the measured eddy diffusivity, and the natural variability of a turbulent atmosphere. Ozone concentrations are good to +/- 5 ppb for IFC-1, and +/- 3 ppb for IFC-2 and IFC-3.

10.2.3 Measurement Error for Parameters

None given.

10.2.4 Additional Quality Assessments

None given.

10.2.5 Data Verification by Data Center

BORIS staff processed the data by:

- Reviewing the initial data files and loading them online for BOREAS team access.
- Designing relational data base tables to inventory and store the data.
- Loading the data into the relational data base tables.
- Working with the TGB-10 team to document the data set.
- Extracting the standardized data into logical files.

11. Notes

11.1 Limitations of the Data

Peroxide deposition velocities at OJP are subject to some uncertainty (factor of 2) simply because we do not know for certain that the application of Kh is appropriate for peroxide transport. The eddy diffusivity for water vapor over OJP was lower than that of heat. Therefore, average peroxide deposition velocities should probably be taken as an upper limit.

11.2 Known Problems with the Data

None given.

11.3 Usage Guidance

Peroxide deposition rates are extremely difficult to measure in the field. Individual measurements of peroxide deposition velocity hold little significance due to the uncertainties mentioned in Section 10.2. However, because of the large amount of data collected, these deposition rates are a valuable component of the peroxide budget. Vd data should be used to assess average deposition rates to a rough, boreal pine forest.

11.4 Other Relevant Information

None given.

12. Application of the Data Set

The data can be used to examine (a) the role of biogenic hydrocarbon emissions with respect to carbon cycles in the boreal forest, (b) the chemical fate of boreal biogenic emissions, (c) the hypothesis that biospheric VOC emissions contribute to peroxide formation, and (d) the deposition rates of hydrogen peroxide and organic peroxides.

13. Future Modifications and Plans

None.

14. Software

14.1 Software Description

All software used to gather data were off-the-shelf, standard scientific scientific packages.

14.2 Software Access

None given.

15. Data Access

The TGB-10 VOC data are available from the Earth Observing System Data and Information System (EOSDIS) Oak Ridge National Laboratory (ORNL) Distributed Active Archive Center (DAAC).

15.1 Contact Information

For BOREAS data and documentation please contact:

ORNL DAAC User Services
Oak Ridge National Laboratory
P.O. Box 2008 MS-6407
Oak Ridge, TN 37831-6407
Phone: (423) 241-3952
Fax: (423) 574-4665
E-mail: ornldaac@ornl.gov or ornl@eos.nasa.gov

15.2 Data Center Identification

Earth Observing System Data and Information System (EOSDIS) Oak Ridge National Laboratory (ORNL) Distributed Active Archive Center (DAAC) for Biogeochemical Dynamics http://www-eosdis.ornl.gov/.

15.3 Procedures for Obtaining Data

Users may obtain data directly through the ORNL DAAC online search and order system [http://www-eosdis.ornl.gov/] and the anonymous FTP site [ftp://www-eosdis.ornl.gov/data/] or by contacting User Services by electronic mail, telephone, fax, letter, or personal visit using the contact information in Section 15.1.

15.4 Data Center Status/Plans

The ORNL DAAC is the primary source for BOREAS field measurement, image, GIS, and hardcopy data products. The BOREAS CD-ROM and data referenced or listed in inventories on the CD-ROM are available from the ORNL DAAC.

16. Output Products and Availability

16.1 Tape Products

None.

16.2 Film Products

None.

16.3 Other Products

These data are available on the BOREAS CD-ROM series.

17. References

17.1 Platform/Sensor/Instrument/Data Processing Documentation
None given.

17.2 Journal Articles and Study Reports
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Sellers, P.J., F.G. Hall, R.D. Kelly, A. Black, D. Baldocchi, J. Berry, M. Ryan, K.J. Ranson, P.M. Crill, D.P. Lettenmaier, H. Margolis, J. Cihlar, J. Newcomer, D. Fitzjarrald, P.G. Jarvis, S.T. Gower, D. Halliwell, D. Williams, B. Goodison, D.E. Wickland, and F.E. Guertin. 1997. BOREAS in 1997: Experiment Overview, Scientific Results and Future Directions. Journal of Geophysical Research 102(D24): 28,731-28,770.

17.3 Archive/DBMS Usage Documentation
None.

18. Glossary of Terms

None.

19. List of Acronyms

```
ASCII   - American Standard Code for Information Interchange
BOREAS  - BOReal Ecosystem-Atmosphere Study
BORIS   - BOREAS Information System
CD-ROM  - Compact Disk-Read-Only Memory
DAAC    - Distributed Active Archive Center
DNPH    - dinitrophenylhydrazine
EOS     - Earth Observing System
EOSDIS  - EOS Data and Information System
GIS     - Geographic Information System
GMT     - Greenwich Mean Time
GSFC    - Goddard Space Flight Center
HPLC    - High Performance Liquid Chromatography
HTML    - Hyper-Text Markup Language
HYD     - Hydrology
IFC     - Intensive Field Campaign
NAD83   - North American Datum of 1983
NASA    - National Aeronautics and Space Administration
NIST    - National Institute for Standards and Technology
NMHC    - Non-Methane Hydrocarbon
NSA     - Northern Study Area
OA      - Old Aspen
OBS     - Old Black Spruce
OJP     - Old Jack Pine
ORNL    - Oak Ridge National Laboratory
PANP    - Prince Albert National Park
REA     - Relaxed Eddy Accumulation
SI      - System International
SSA     - Southern Study Area
TF      - Tower Flux
TGB     - Trace Gas Biogeochemistry
URL     - Uniform Resource Locator
VOC     - Volatile Organic Compound (or Carbon)
WSU     - Washington State University
```

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The BOREAS TGB-10 team collected several trace gas data sets in its efforts to determine the role of biogenic hydrocarbon emissions with respect to boreal forest carbon cycles. This data set contains measured VOC concentrations. These data were obtained at the SSA-OJP site from May to September 1994. The data are stored in tabular ASCII files.

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